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"RADIATIVE PROPERTIES OF ASH AND SLAG"

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ABSTRACT

The objective of this program has been to make laboratory measurements of the radiative properties of ash and slag deposits that have been extracted from combustion devices. The program has resulted in measurements of radiative properties of materials at high temperatures made by a technique employing a sample heating device that is coupled to a FT-IR spectrometer to measure emission, directional-hemispherical transmission, and directional-hemispherical reflection of a sample. By this technique, the temperature at the measurement point and the spectral emittance (emissivity) of the surface are both obtained. These measurements are then related to the physical and chemical properties of the surface to determine what controls the radiative properties. The measurements have shown that the physical state of a deposit (i.e. fused, sintered or packed particles) greatly influence the measured spectral emittance.

The main accomplishments of the program are as follows:

- Demonstration of measurement technique validation.
- Measurements of spectral emittance for deposit samples as a function of temperature and morphology.
- Accurate calculations of the optical properties of smooth and sintered surfaces based on the material's complex index of refraction and the surface morphology.

RADIATIVE PROPERTIES OF ASH AND SLAG

Contract No. D01AC22-87PC79901

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Final Report

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I. INTRODUCTION

I.1. Relation to DOE Mission

This project relates to the Department of Energy's interest in the "Critical Properties Affecting Radiant Heat Transport" in combustion systems. Thermal radiation plays a key role in the operation and efficiency of combustion systems, accounting for over 90% of the heat transfer. The radiative heat transfer in coal-fired boilers is dominated by the properties of inorganic deposits and bounding surfaces, and of particulates, which are present in the system. The properties governing the emission, absorption, and attenuation of the radiative energy by deposits and entrained particulates are a key element in accurately predicting the radiative heat transfer. They are also necessary for in-situ determination of current deposit condition (composition and temperature) from optical measurements. As the need increases for higher efficiency and better pollution control, more complete knowledge of the boiler operating conditions is necessary. Thus, there is an increased need to know the radiative properties of deposits and particulates in coal fired combustion systems. This project has resulted in measurement of these properties for collected ash and slag samples and an understanding of the factors which affect the radiative properties.

I.2. Specific Project Objectives

The objective of this program has been to make laboratory measurements of the radiative properties of ash and slag deposits that have been extracted from combustion devices. The program has resulted in measurements of radiative properties of materials at high temperatures made by a technique employing a sample heating device that is coupled to a FT-IR spectrometer to measure emission, directional-hemispherical transmission, and directional-hemispherical reflection of a sample. By this technique, the temperature at the measurement point and the spectral emittance (emissivity) of the surface are both obtained. These measurements are then related to the physical and chemical properties of the surface to determine what controls the radiative properties. The complex index of refraction that is required to calculate emissivities is determined by a transmission spectroscopic technique that employs fine sample particulates suspended in KBr and CsI matrices.

I.3. Technical Project Objectives

Knowledge of the optical properties of ash and slag deposited on boiler tube surfaces from the combustion of coal is necessary for a thorough understanding of furnace operation. These properties are amongst the inputs needed to characterize the rate of transfer of energy between surfaces and flames. They are also necessary for in-situ determination of current slag condition (composition and temperature) from optical measurements.

A precision measurement of the high temperature optical properties of ash and slag requires that the sample temperature at the time of measurement be known. For surfaces at high temperature the emitted spectrum of electro-magnetic radiation is the most convenient probe of temperature if the spectral emittance of the sample is known at that temperature. This emittance depends on the surface and subsurface composition and topologies, as well as on the temperature. At present, the spectral emittance cannot be calculated for an arbitrary surface at an arbitrary temperature; it must be measured.

There are two basic methods for measuring the spectral emittance (1): i) measurement of the radiation emitted from the surface at a known temperature (spectral emittance) and ii) measurement of radiation reflected from, and transmitted through the material (1 - spectral emittance). Both methods have been applied to the measurement of emittances at high temperature (2-12). The emission method suffers from problems associated with distinguishing emitted radiation from furnace radiation reflected from the surface. The minimization of such reflected radiation can result in the loss of precise control and knowledge of sample temperature, which is necessary for the determination. The exception

is the case of samples which can be inserted into or be fashioned into thin walled tubes and heated electrically (2-5).

In the reflection method, external radiation is reflected from the surface. It is modulated to distinguish it from the emitted or reflected furnace radiation. The reflected radiation must be measured over all angles of reflection, and this limits the degree to which the sample can be surrounded by the furnace. Again, precise knowledge of the sample temperature must be sacrificed to gain optical access.

This program proposed that many of the problems of measuring emittance and temperature could be overcome by using both the radiance and reflectance/transmittance methods simultaneously in a geometry which eliminates any reflected furnace radiation. The reflectance measurement would be used to determine the sample emittance but at an imprecisely known temperature. The emittance would then be used in conjunction with the measurement of emitted radiation to determine the temperature. Therefore, both the emittance and temperature would be determined.

An objective of this program was to implement and test this concept using an apparatus consisting of a furnace, optics and a Fourier Transform Infrared (FT-IR) Spectrometer. We intended to prove the feasibility of making spectral emittance measurements in the mid IR, 1.6 to 20 microns, at moderate sample temperatures for a number of calibration samples. After technique validation, the method would be applied to the required ash and slag deposits. We were to determine the spectral emittance at nearly normal incidence both from integrated measured directional reflectance (specular and diffuse) and measurement of the radiance from a surface.

There are four features of FT spectrometers which are ideal for this purpose: 1) FT spectrometers modulate their source radiation; each source frequency has a unique modulation frequency. The detector is sensitive only to the modulated radiation, so that the unmodulated emitted and reflected furnace radiation do not interfere with the measurement. This feature eliminates the need for chopping in a reflectance measurement and allows simultaneous detection at all frequencies. 2) FT spectrometers are fast and sensitive because they measure all frequencies simultaneously (a complete radiance spectrum was collected in 0.11 sec). 3) FT spectrometers can measure both emission and reflection simultaneously. 4) The FT computer can be employed to measure other outputs of the experiment and supply control functions based on these outputs or the measured spectra. These properties, together with the speed, computing power and relatively low cost of modern FT spectrometers make an FT based instrument for measuring radiative properties very attractive.

In addition to the laboratory radiative property measurements of ash and slag at elevated temperatures, the complex index of refraction was determined by transmission techniques employing fine particles of the materials suspended in KBr and CsI matrices. Emissivities were then calculated by three considered models to compare with the observed emittances.

All acquired ash and slag samples were also characterized by FT-IR transmission spectroscopy and compositional x-ray analysis for ground samples.

1.4. Summary of Project Accomplishments

- Success in constructing an optical apparatus that provides transfer and collection optics for measuring directional reflectance (specular and diffuse), transmittance, and radiance from a surface at temperatures up to 2226 K.
- Identification using the reflectance and transmittance of a spectral region for many materials (including slags) where they exhibit essentially no reflectivity or transmittivity, thereby defining the emissivity to be 1.0 at this spectral region.

This phenomenon has been identified as the Christiansen dip. The surface temperature can be determined directly from the radiance measurement at this region, which then allows for the calculation of the entire spectral emittance.

- **Determination of the spectral emittance as calculated from the measured directional-hemispherical reflectance and transmittance (closure) and use of this emittance to determine the sample temperature from the radiance.**
- **With both the Christiansen dip and closure methods, there is good agreement between the emissivities and temperatures determined by the two methods.**
- **Excellent agreement for many of the calibration samples between our determined spectral emittance and results from other investigators.**
- **Measurements of spectral emittance for deposit samples as a function of temperature and morphology.**
- **The morphology is very important in determining the samples reflectivity in regions where the absorption is weak. Here a higher direction-hemispherical reflectivity can be achieved for sintered samples than for smooth samples because of reflection from the many surfaces in the sintered sample.**
- **Measurement of the complex index of refraction for deposit samples.**
- **Accurate calculations of the optical properties of smooth and sintered surfaces based on the material's complex index of refraction and the surface morphology.**

II. EXPERIMENTAL AND TECHNIQUE VALIDATION

II.1. Apparatus

A schematic of an FT-IR spectrometer, coupled with our apparatus that provides the transfer and collection optics for measuring directional reflectance (specular and diffuse) and radiance from a surface is shown in Fig. II.1.1.

Reflectance and Transmittance - For the reflectance measurement (Fig. II.1.1a), the FT-IR spectrometer's source radiation is directed through the interferometer where it is modulated, then directed to a stationary mirror located near the outer edge of the rotating optical table. This stationary mirror is an off-axis parabolic mirror having an acceptance angle of $26\frac{1}{2}^\circ$ and a 12" effective focal length. The modulated IR radiation is focused onto the surface of interest and is then collected by a matching $26\frac{1}{2}^\circ$, 12" effective focal length off-axis parabolic mirror that is secured to the rotating table. From here the radiation is focused onto a detector that is sensitive to the modulated radiation.

Defining the center of the incident IR beam to be 0° , the center of the collected beam can be positioned at any angle from $\theta = 15^\circ$ to $\theta = 195^\circ$. Since the width of the mirror is 5° , the radiation emittance around the circle can be determined by taking data every 5° . With this range of rotation, the transmittance of partially transparent materials can also be determined. $\theta = 15^\circ$ corresponds to the specular reflection angle for all samples studied.

Radiance - For radiance measurements, the radiation emitted from a hot sample surface is collected by the stationary mirror and directed backwards through the FT-IR spectrometer's interferometer to an emission detector (Fig. II.1.1b).

Sample Holder - A schematic of the sample holder is shown in Fig. II.1.2. To hold and precisely position the samples, three $6" \times 3/4" \times 0.35"$ spring steel reciprocating saw blades with modified cobalt steel teeth were connected to a $1\frac{1}{2}"$ square positioning mount (Daedal, Inc.). The two fine resolution positioning screws allowed for precise tilting of the sample surface in two directions. The saw blades were placed close enough to each other so that they would have to be stretched apart to place a sample between them. The combination of the resultant inward force from the resiliency of the spring steel and the gripping action of the teeth locked the sample into position. Test materials for technique validation were discs, squares and irregular shapes ranging from $3/4"$ to $2"$ from edge to edge for the surface directed at the collection optics. Typically, a sample would be aligned for reflectance measurements at room temperature by monitoring the intensity of the reflected radiation at the specular angle. It would then be brought to elevated temperature, and then re-positioned, if necessary, to account for any slight sample movement due to thermal expansion effects on the sample or saw blades.

The sample holder held up well under all heating conditions. By gripping the samples so that no part of the holder was in front of the sample, extraneous radiation from the hot surfaces of the holder could be eliminated from the radiation collection optics.

Sample Heating - Heating of the samples was accomplished by either a hydrogen/oxygen flame produced from a premixed burner (McKenna Products, Inc.) that was placed in the center of the rotating table and directly below the sample (Fig. II.1.3), or by heating the back of the sample (as shown in Fig. II.1.2) with either a propane or an acetylene/oxygen torch. A complication resulted from surrounding the sample with the H_2/O_2 flame. This was the emission and absorption line spectra of the IR active gases of the reaction product of the flame, H_2O . However, at sufficiently high resolution ($\leq 0.5\text{ cm}^{-1}$) these lines do not overlap, permitting a continuum spectrum to be determined at the baseline of the H_2O line spectrum. By back heating and providing a slight exhaust ventilation directly above the sample, contributions from hot water vapor were negligible, and slight changes in the CO_2 level in the beam path allow for easy extrapolation to a continuum spectrum.

Figure II.1.1. Schematics of Optical Paths for a) Reflectance and Transmittance Measurements and b) Radiance Measurements.

Figure II.1.2. Schematic of Sample Holder.

Figure II.1.3. Side View of Rotating Table with Premixed Burner for Sample Heating.

Of the three heating techniques used, the acetylene/oxygen torches achieved the hottest surface temperatures, up to 2226 K, at this point.

II.2. Measurement Techniques

Radiation incident on a slab of material, as shown in Fig. II.2.1, is either reflected, absorbed or transmitted:

$$\rho_{\nu} + \alpha_{\nu} + \tau_{\nu} = 1 \quad (1)$$

where ρ is the fraction of radiation reflected, α the fraction absorbed, τ the fraction transmitted, and where the subscript ν indicates a spectral quantity. This fact, a statement of energy conservation, is true for samples with either optically smooth or rough surfaces, and is the basis for the method that we present for the measurement of emittance and temperature of a surface.

By a Kirchoff analysis it can be shown that the emissivity, ϵ , is equal to the absorptivity, α (1).

$$\epsilon_{\nu} = \alpha_{\nu} \quad (2)$$

The suffix "ivity" is used here for all surface types, as discussed by Siegel and Howell (13).

For this method we must determine ρ_{ν} , τ_{ν} , and ϵ_{ν} , experimentally. The validity of the measurements will be checked by closure, i.e., the determined values of ρ , α , and τ must add to unity (Eqs. 1 and 2).

Measurements required to determine these quantities are: the radiance from the surface, compared with that of a black-body at a known temperature; the reflectivity, ρ_{ν} , and the transmittivity, τ_{ν} .

For opaque slabs ($\tau = 0$), we have that

$$\rho_{\nu} + \epsilon_{\nu} = 1 \quad (3)$$

In the application of Eqs. 1 and 2 to a given problem we must be more specific about the definitions. For a directional input beam, the reflectivity referred to for the general case of Eq. 1 is the direction-hemispherical spectral reflectivity (2). This concept is illustrated in Fig. II.2.2, where a collimated beam is incident on the sample, and the radiation reflected into the complete reflection hemisphere defines the direction-hemispherical spectral reflectivity. Likewise, the transmittivity is the direction-hemispherical spectral transmittivity, and the emissivity is the directional spectral emissivity (14). These concepts are also illustrated in Fig. II.2.2. Measurement of the directional emissivity would be made for outgoing radiation at

only one angle. The direction of this outgoing radiation will be antiparallel to the incident beam shown in Fig. II.2.2.

The disposition of the sample, optics, and heating techniques are such that direct measurements of hemispherical properties with this apparatus are not possible. For radiation incident normally on the sample, measurement of the bi-directional reflectivity in the θ plane is sufficient to characterize the reflectivity over the complete reflection hemisphere if the sample is an isotropic scatterer. In our experiments the radiation will be incident at a direction very close to the surface normal. In that case, "integration" of the measured bi-directional reflectivity and transmittivity overall all angles of the hemisphere will yield the required directional-hemispherical properties for isotropic scatterers (2). In doing this we make use of well known reciprocity relationships (2).

Reflection and Transmission - To make quantitative measurements, the FT-IR reflection and transmission experiments require normalizing the sample spectrum with a reference (or

Figure II.2.1. Schematic Showing That Radiation Incident on a Slab of Material is Either Reflected, Absorbed or Transmitted.

Figure II.2.2. Diagram Showing a Possible Disposition of Energy in a General Experiment in which Incident Energy is Either Reflected, Absorbed or Transmitted.

background) spectrum. For reflectance measurements, a first surface gold mirror (totally reflecting) was placed at the sample position but mounted to rotate so that the specularly reflected beam can be focused onto the detector for all detector angles. This allows for a reference spectrum to be taken at each collection angle θ . Figure II.2.3 shows the detector response at several collection angles and the optical efficiency or deviation through these angles. Typically the deviation around the optical table is less than $\pm 2\%$. A reference spectrum at $\theta = 180^\circ$ can be taken in the absence of the gold mirror. Each angular measurement of reflected or transmitted radiation can then be normalized by a reference spectrum to indicate what percentage of the available incident radiation was detected in each angular direction. Figure II.2.4 shows typical reflection measurements from polished and rough silicon nitride. The polished surface is essentially a specular reflector with negligible energy being detected at $+ 5^\circ$ from specular and no energy being detected at larger angles. The rough surface, however, exhibited non-specular components of energy out to $\theta = 75^\circ$.

The optics and the computational routine developed to obtain the radiation integrated over a hemisphere allows for measurements to be taken at $+ 5^\circ$ intervals from specular. The area of each angular hemispherical component corresponding to each angular measurement (see Fig. II.2.5) can be calculated from

$$\text{Area} = \int_{\theta' - 2.5^\circ = \theta'_1}^{\theta' + 2.5^\circ = \theta'_2} 2 \pi r^2 \sin \theta' d\theta' \quad (4)$$

$$= 2 \pi r^2 (\cos \theta'_1 - \cos \theta'_2) \quad (5)$$

where $\theta' = 0$ for the specular measurement.

For the specular component:

$$\text{Area}_{\text{specular}} = \int_{\theta' = 0}^{\theta' + 2.5^\circ} 2 \pi r^2 \sin \theta' d\theta' \quad (6)$$

$$= 2 \pi r^2 (1 - \cos 2.5^\circ) \quad (7)$$

The scale factors used to convert each angular measurement to a hemispherical component were calculated from the ratio of

$$\text{Scale factor} = \frac{\text{Area}}{\text{Area}_{\text{specular}}} = \frac{2 \pi r^2 (\cos \theta'_1 - \cos \theta'_2)}{2 \pi r^2 (1 - \cos 2.5^\circ)} \quad (8)$$

These factors were applied to the spectra shown in Fig. II.2.4. The total integrated radiation over the hemisphere is then obtained by taking the sum of the angular hemispherical components.

Emission - The optical path and emission detector used for the radiance measurements were calibrated for energy losses and responsivity by placing a black-body cavity emitter at the sample location. Figure II.2.6 shows the energy response of the emission detector to the black-body cavity at 1090 K, the theoretical radiance calculated by the Planck radiation formula for a black-body at 1090 K, and the ratio of the observed to theoretical radiance, which serves as our instrument response function for radiance measurements. Room temperature background radiation was also accounted for in the radiance measurements.

Test Samples for Technique Validation - The test samples used, for technique validation, in this program are listed in Table 1. A wide range of materials and surface topologies were tested to demonstrate the versatility and global application ability of our spectroscopic technique for measuring spectral emittance and surface temperature. Data for samples #1-3

Figure II.2.3. a) Detector Response to FT-IR Source Collected After Reflecting Off a First Surface Gold Mirror at $\theta = 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$ and 90° (there are six overlaid radiance spectra of the FT-IR source in this figure) and b) Optical Efficiency Calculated by the Ratio of θ/θ_{15° .

Figure IL.2.4. Reflectance Components of Polished Si₃N₄ (a-b) and Several Reflectance Components of Rough Si₃N₄ (c-g).

Figure II.2.5. Diagram Showing Schematic of Boundaries used for Calculating Angular Hemispherical Components from Angular Measurements in the Reflection Hemisphere. The Hemispherical Component Shown is at the Collection Mirror Position $+20^\circ$ from the Specular Angle.

Figure IL2.6. a) Energy Response of the Emission Detector to a Black-body Cavity at 1090K, b) Theoretical Radiance for a Black-body at 1090K, and c) Radiance Instrument Response Function = Ratio of Observed to Theoretical Radiance.

TABLE 1: SAMPLES STUDIED

Sample No.	Material	Supplier	Designation	AFR Sample Class	Surface Temperature(s), K
1	Si ₃ N ₄ (polished)	Cercom, Inc.	Bearing Grade "PAD" LP B-phase 2" x 2" x 0.31" thick	A	300, 925, 1025, 1475
2	Si ₃ N ₄ (surface ridges)	Cercom, Inc.	Bearing Grade "PAD" LP B-phase 2" x 2" x 0.31" thick	B	800, 1040
3	Si ₃ N ₄ (sand blasted)	Cercom, Inc.	Bearing Grade "PAD" LP B-phase 2" x 2" x 0.31" thick	A	1050
4	Si ₃ N ₄ (surface ridges)	Norton, Co.	Noralid NC-132 B-phase 1" x 1" x 0.063" thick	B	1050
5	Fused Quartz	Esco Products	Optical Grade 1.5" dia. x 0.125" thick	A	300, 906
6	Synthetic Sapphire	Esco Products	Optical Grade 1.125" dia. x 0.125" thick	A	965
7	Al ₂ O ₃	Coors Ceramics	0.998 2" dia. x 0.125" thick	C	1415
8	Al ₂ O ₃	McDaniel Refractory Company	0.998 1.25" dia. x 0.188" thick	C	800-2226
9	Shuttle AFRSI	Arnold Eng. Dev. Center	Woven Quartz Fiber Quilt 1.5" x 0.5" thick	C	682
10	Stainless Steel Pipe Plug	Cajon Co.	Type 316 1" NPT	D	300, 758, 1023
11	Anodized Aluminum	Nicolet Instruments	1.5" x 1.5" x 0.5" thick	C	712
12	Aluminum (surface ridges)	Mohawk Aluminum	Type 6061 1" x 1.5" x 0.5" thick	E	300
13	Aluminum (sand blasted)	Mohawk Aluminum	Type 6061 1" x 1.5" x 0.5" thick	D	758
14	Alumina- Silica- Magnesium Ceramic	Arnold Eng. Dev. Center	1.25" x 1.25" x 0.25" thick	C	1120
15	SiC (surface ridges)	Carborundum Co.	2" x 0.75" x 0.125" thick	B	1075, 1421

Data for samples number 1-3 and 9-15 were taken under U.S. DOD Contract No. F40600-88-C0011

and 9-15 were taken under a separate program (U.S. DOD Contract No. F40600-88-C0011), but is also reported here as it is good validation data for the measurement techniques.

II.3. Measurement Technique Validation: Analysis

Determination of Surface Emittance and Temperature Using Closure - From Eqs. 1 and 2 the spectral emittance from reflectance/transmittance measurements was calculated by

$$\epsilon_{\nu} = 1 - \rho_{\nu} - \tau_{\nu} \quad (9)$$

Figure II.3.1a-b shows the measured hemispherical reflectance and the spectral emittance calculated by Eq. 9 for an opaque slab ($\tau_{\nu} = 0$) of polished silicon nitride at elevated temperature. A radiance measurement, corrected for instrument response and background is shown in Fig. II.3.1c.

If the surface temperature is known, a spectral emittance can be calculated from the radiance measurement, R_{ν} , by

$$\epsilon_{\nu} = R_{\nu}/BB(T)_{\nu} \quad (10)$$

where $BB(T)$ is the theoretical black-body radiance corresponding to the surface temperature, (T) .

Rearrangement of Eq. 10 will allow us to calculate a temperature spectrum from the radiance measurement and the spectral emittance determined from the reflectance measurement, that is,

$$BB(T)_{\nu} = R_{\nu}/\epsilon_{\nu(1-\rho_{\nu}-\tau_{\nu})} \quad (11)$$

Figure II.3.1d is of the temperature spectrum calculated by Eq. 11 using Figs. II.3.1b and II.3.1c as inputs. Figure II.3.1e overlaps the calculated temperature spectrum with a theoretical black-body radiance spectrum corresponding to 1025 K. A good "fit" is demonstrated, indicating that the surface of the silicon nitride slab was at a temperature of 1025 K. Figure II.3.1f shows that temperature deviations of ± 10 K in the theoretical black-body radiance calculation are easily determined not to "fit" the experimentally measured surface temperature.

Once the surface temperature has been determined, Eq. 10 can be used to recalculate the spectral emissivity. The result, as shown in Fig. II.3.2 should compare well with the spectral emittance determined from the reflectance closure. A comparison is shown in Fig. II.3.2b. Recalculating the spectral emissivity may be useful if the emittance determined by closure is particularly noisy in any spectral regions, since the theoretical black-body radiance spectrum is noise free and the surface radiance spectrum typically has a high signal to noise ratio.

To summarize the closure technique for determining surface emittance and temperature, five steps are required:

1. Measure the reflected and transmitted IR radiation as a function of angle around a hot sample.
2. Calculate the hemispherical reflectance/transmittance.
3. Apply closure (Eq. 9) to determine the spectral emittance.
4. Measure the radiance (at one angle) from the hot surface.
5. Determine the surface temperature (Eq. 11) from the radiance measurement and the spectral emittance determined by closure.

Figure II.3.1. Sequence for Spectral Emittance and Surface Temperature Measurement from Reflectance Closure and Radiance Measurement for Polished Si₃N₄. a) Integrated Hemispherical Reflectance, b) Emittance = 1-Reflectance, c) Radiance, d) Surface Temperature Spectrum = Radiance/ $\epsilon_{1\text{-Reflection}}$ and e-f) Surface Temperature Determination by Overlaying with Best-fit Theoretical Black-body Temperature Curves. T_{Surface} = 1025K.

Figure II.3.2. a) Spectral Emittance Re-calculated with Eq. 10 from the Radiance Measurement (Fig. II.3.1c) and the Surface Temperature Determined by Reflectance Closure (Fig. II.3.1e), and b) Re-calculated Spectral Emittance Compared with the Spectral Emittance Determined by Reflectance Closure (Fig. II.3.2a compared with Fig. II.3.1b).

6. (Optional) Recalculate the spectral emittance (Eq. 10) with the radiance measurement and the surface temperature determined in Step 5.

Determination of Surface Temperature and Emittance Using the Christiansen Dip - A more accurate determination of surface temperature would be from the radiance measurement at a spectral region where the emittance is known to be 1.0. At this spectral region R_ν and $BB(T)_\nu$ must coincide, and once the temperature is determined, the entire spectral emittance can be determined.

For many of our test samples, the reflectance/transmittance measurements indicated a spectral region where there was absolutely no reflected or transmitted energy. Figure II.3.3. shows this point for the opaque slab ($\tau_\nu = 0$) of silicon nitride to be at 1206 cm^{-1} . This spectral region can be attributed to the Christiansen Effect (15), which is when the real part of the refractive index of the material is 1 (air = 1) and the imaginary part is low. Under these conditions almost no reflection will be observed. Reflectance for opaque slabs can be described by

$$R = \frac{[(n - 1)^2 + k^2]}{[(n + 1)^2 + k^2]} \quad (12)$$

where n is the real part of the refractive index and k is the imaginary part. n and k determine the phase velocity and the attenuation of the wave as it propagates through the medium, respectively. Figure II.3.4, taken from Ref. (15) demonstrates the Christiansen effect for silicon carbide where $n = 1$ and $k \approx 0$. When $n = 1$, $R = k^2/[(n + 1)^2 + k^2]$ which can be very small for small values of k . When $n = 1$ and k is as small as 0.1, however, $R = 0.002$ and $1 - R = \epsilon = 0.998$. The emittance deviates from 1.0 by only a fraction of a percent. For small values of k , one might think that the majority of the propagating wave would pass through the sample, but even small values of k produces substantial attenuation (absorption) by the medium. The attenuation of radiation is given by $I = I_0 e^{-(4\pi k/\lambda)t}$, so for $k = 0.1$ at $10 \text{ } \mu\text{m}$ wavelength, the incident radiation is attenuated by $1/e$ in a distance of $0.8 \times 10^{-2} \text{ mm}$. For example, in coal, $k < 0.05$ over most regions of the infrared spectrum between 400 cm^{-1} to 4000 cm^{-1} (16,17), but significant absorption occurs with a thickness on the order of $0.8 \times 10^{-2} \text{ mm}$ (18).

In optically thin samples, the Christiansen effect can be exploited to make a band pass filter (19), but for our purpose, it defines a spectral region where $R = 0$ and $\epsilon_\nu = 1.0$, thus allowing a fast and accurate method of determining the surface temperature and spectral emittance.

Figure II.3.5a overlays the silicon nitride radiance spectrum (same as Fig. II.3.1c) with a theoretical black-body radiance that coincides where $\epsilon_\nu = 1.0$, as determined by the reflectance measurement. The temperature used to calculate the theoretical radiance was 1025 K, the same surface temperature arrived at by the reflectance closure technique. A spectral emittance can also be calculated from the radiance measurement and the surface temperature obtained via the Christiansen dip, Fig. II.3.5b, and again, corresponds very well with the spectral emittance determined by reflectance closure (Fig. II.3.1b).

To summarize the Christiansen dip technique for determining surface temperature and emittance, four steps are required.

1. Determine if a material exhibits a Christiansen dip (i.e., a spectral region where the reflectance goes to zero from a reflectance measurement at one angle. A transmission measurement may also be necessary to confirm that the material is opaque at the Christiansen dip region.
2. Measure the radiance (at one angle) from the hot surface.

Figure II.3.3. Opaque Slab ($\tau_v = 0$) of Silicon Nitride Showing Spectral Region of Zero Reflectance and Transmittance at 1206 cm^{-1} . a) Reflectance at the Specular Angle and b) Same as (a) with Expanded Scale.

Figure II.3.4. a) Reflectance and b) Optical Constants for Silicon Carbide, Taken from Ref. (15), Demonstrating Christiansen Effect when $n=1$ and $k \approx 0$.

Figure II.3.5. Surface Temperature and Spectral Emittance of Cercom Polished Silicon Nitride Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Radiance Overlaid with a 1025K Theoretical Black-body Curve and b) Emittance = Radiance/ $\text{BB}_{1025\text{K}}$.

3. Match the Christiansen dip spectral region in the measured radiance spectrum with a theoretical black-body radiance; this determines the surface temperature.
4. Calculate the entire spectral emittance (Eq. 10) from the radiance measurement of the hot surface and the theoretical black-body radiance that corresponds to the determined surface temperature.

The Christiansen dip method also serves as verification of the spectral emittance determined by closure. Also to be used to verify closure will be values cited in the literature for spectral emittance, and comparison of spectroscopically determined surface temperature to thermocouple indications. For many of the samples used in this program, a 0.005" diameter fine wire thermocouple was bonded to the sample's surface next to where the IR beam was focused. Internally placed (in a blind hole) and externally touched thermocouples were also monitored.

For materials that exhibit a Christiansen dip, this technique in its own right is a worthwhile method for accurately measuring surface temperature and spectral emittance. Only one reflectance measurement is required to indicate where $\epsilon_v = 1.0$, and then the radiance measurement is taken. We have demonstrated that the spectral region of zero reflectance/transmittance is maintained over all collection angles.

II.4. Measurement Technique Validation: Results

Classes of Samples - Our FT-IR reflectance/transmittance spectroscopic technique allowed us to identify basic differences in the way materials and surfaces would reflect, transmit, or scatter the incident IR radiation. Based on these difference, we developed an analysis and classification scheme that would have application to any material tested in our apparatus.

As shown in Fig. II.4.1, materials can be either specular or diffuse reflectors. Diffuse reflectors are further separated into surfaces that isotropically or anisotropically reflect the incident radiation.

Surfaces are also identified as to their ability to transmit the incident radiation into the subsurface. There is a frequency dependence for the transmittance classification, however. Fused quartz, for example, is partially transmitting only over part of the spectrum. Also, materials are classified according to whether or not a Christiansen dip is observed. From our observations, we have estimated the relative "in the field" sizes of each classification and indicated this by proportionally sizing the upper part of Fig. II.4.1.

For each sample type, an identification was made of how emissivity can be obtained. This determines the sample "class" which is indicated by shading, crosshatching, etc. In the lower part of this figure, each sample "class" is listed with the appropriate method(s) for determining surface emittance and temperature, and an accuracy rating based upon the method(s) used. Overlap of methods (i.e., applying both closure and Christiansen dip techniques) would result in the highest accuracy since the two separate methods should arrive at the same emittance and temperature.

To experimentally determine a sample "class", we first identified whether a sample was a specular or a diffuse reflector. If it was a diffuse reflector, it was then necessary to determine if the surface was isotropically or anisotropically reflecting the incident radiation. For surfaces with ridge patterns that originated in the manufacturing process ("grains" due to cutting or press patterns), typically anisotropic reflection was observed. This was determined by measuring the hemispherical reflectivity, and then repeating the measurement at different rotational orientations of the sample with respect to the plane of incident and collected IR radiation. For isotropically reflecting surfaces, each orientation should produce the same result. For anisotropically reflecting surfaces, each orientation will produce a distinct

Figure II.4.1. Analysis Scheme for Radiative Property Determinations of Solid Surfaces.

"directionally influenced" integrated hemispherical reflectivity. By averaging the "directionally influenced" measurements, closure can be demonstrated.

In our classification scheme, partially transmitting does not only refer to those materials that transmit energy through the sample and so require quantitative transmittance measurements to establish closure. It also applied to samples that are thick enough to be optically opaque, but that allow the incident IR beam to propagate to a penetration depth that causes internal scattering effects, if present, to be detrimental to the closure measurement. Polycrystalline Al_2O_3 (alumina ceramic) was one sample to present this effect. Reflectance and transmittance measurements resulted in a calculated ϵ_p that was significantly higher in most spectral regions than ϵ_p from other methods (i.e., the reflectance/transmittance measurement was "missing" much of the radiation). Figure II.4.2a is a photograph of the Al_2O_3 surface with a 1 mm diameter He-Ne laser beam being reflected off of the surface. The diameter of the resultant red spot is more than 10 times greater than that of the incident beam. Some widening would be expected due to the rough, diffuse reflecting surface of the material, but the extent of the widening and the observation that the transmitted red laser light produced a spot of equal large diameter on the anterior side of the Al_2O_3 , confirmed that internal multiple scattering of the light was occurring.

This multiple scattering effect will allow radiation that propagates into the material to emerge from the same surface, but effectively enlarging the outgoing spot size with respect to the incident spot size. When this occurs, a significant amount of the outgoing radiation will not be directed into the collection angle of our collection optics (Fig. II.4.2b), which is always focused at the same location and size of the incident radiation, resulting in low reflectance/transmittance measurements. Fortunately, the majority of partially transmitting materials will exhibit a Christiansen dip.

Figure II.4.3 demonstrates the interactions of the incident IR radiation with the different classes of materials tested in this program. If a material exhibits a Christiansen dip, the analysis time to determine surface temperature and spectral emittance is greatly reduced. Table 2 compares the typical data collection time used for the closure and Christiansen dip techniques for each sample class. As indicated, the Christiansen dip method required considerably less data collection time for diffuse reflectors since quantitative angular reflectance measurements are not required.

Surface Emittance and Temperature Determinations - One or two examples of each sample class tested will be presented in this section. The complete list of surfaces tested is presented in Table 1. Additional data are presented in Appendix A. The optical grade fused quartz, synthetic sapphire, and silicon nitride at temperatures below 1000 K were heated with the H_2/O_2 burner; to reach higher temperatures, these and all other samples were heated from the back or side with either a propane or O_2 /acetylene torch.

Sample Class A

Fused Quartz - Optical grade fused quartz was partially transmitting, specularly reflecting and exhibited a Christiansen dip. With these properties, the spectral emittance and surface temperature was obtainable by both reflectance closure and the Christiansen dip technique. Internal scattering and reflection of the transmitted radiation was apparently a negligible factor since reflectance closure was obtained.

Figure II.4.4 presents the hemispherical reflectance and transmittance for the quartz at room temperature. Also shown is the calculation of spectral emittance by Eq. 9 and a comparison to moderately high temperature data taken by other investigators (20).

In the transmittance spectrum, the decline at 3000 cm^{-1} matches the frequency cut off specifications for IR grade fused quartz. The features at 3650 cm^{-1} and 4500 cm^{-1} are characteristic absorption bands of hydroxyl ion impurities in the quartz.

10 mm

Collection
Focusing
Mirror

Incident
Focusing
Mirror

Figure II.4.2. a) Reflection of 1mm Diameter He-Ne Laser Beam from Surface of Al_2O_3 Ceramic to Demonstrate Internal Multiple Scattering Effects and b) Schematic Showing how these Effects Direct IR Radiation out of Our Collection Optics by Effectively Enlarging the Outgoing Spot Size with Respect to the Incident Spot Size.

Figure II.4.3. Sample Classes with Schematics Showing Interaction of Incident IR Radiation.

TABLE 2: DATA COLLECTION TIME BY SAMPLE CLASS

	Method	Typical Data Collection Time
Class A (specular):	by Closure	< 10 minutes
	by Christiansen dip	< 10 minutes
Class A (diffuse):	by Closure	< 30 minutes
	by Christiansen dip	< 10 minutes
Class B:	by Closure	< 30 minutes
	by Christiansen dip	< 10 minutes
Class C:	by Christiansen dip	< 10 minutes
Class D:	by Closure	< 30 minutes
Class F:	by Closure	< 30 minutes

Figure II.4.4. a) Total Integrated Spectral Reflectivity for Optical Grade Fused Quartz at Room Temperature, b) Transmittance Through the Sample, c) Spectral Emittance Calculated from 1-Reflectance-Transmittance, and d) Data of Myers et al., (20) at 1273K.

Excellent agreement in shape was achieved between the spectral emittance calculated from the reflectance and transmittance measurements with the literature data. Amplitude differences at $\sim 1100\text{ cm}^{-1}$ will be shown to be due to the temperature difference (i.e., room temperature vs 1273 K).

Figure II.4.5 shows the measured hemispherical reflectance and transmittance and the calculated spectral emittance at $\sim 900\text{ K}$. The quartz was brought to elevated temperature by heating from below with the H_2 flame. Overlaid on the emittance spectrum is the literature data from Fig. II.4.4d. Agreement is excellent below 3000 cm^{-1} , in the non-transparent region of the quartz. Differences in the hydroxyl absorption regions are most likely due to concentration differences. Note the discrepancy with our non-zero emittance above 5000 cm^{-1} . This may be an indication that a small component of internal reflection is causing radiation to be directed out of our collection angle for reflectance and transmittance measurements, thus resulting in an elevated emittance.

In the presence of the combustion product of the H_2/O_2 burner (hot water vapor), the radiance measurement (Fig. II.4.6a) was taken at 0.5 cm^{-1} spectroscopic resolution so that a continuum quartz spectrum could be determined at the baseline of the resultant H_2O line spectrum. In the region of the Christiansen dip for the quartz ($\sim 1400\text{ cm}^{-1}$), the surface temperature was determined to be 906 K. A theoretical black-body radiance curve corresponding to 906 K is overlaid on the quartz radiance spectrum. The spectral emittance as calculated from Eq. 10 is shown in Fig. II.4.6c. Again, the hot water vapor spectrum lies on top of the quartz continuum.

The quartz sample has demonstrated that we can determine the spectral emittance and temperature for Class A materials from both the closure and Christiansen dip techniques. Figure II.4.7 compares the emittance from each technique, and very good agreement is shown, given the distraction of the overlying hot water vapor bands.

As when compared to the literature emittance, the closure method is slightly elevated above the Christiansen dip method at the high wavenumber end of the spectrum where quartz is transparent.

Sapphire - The same discrepancy occurred for a synthetic sapphire window (see Figs. A1 and A3 of Appendix A). For the sapphire, the H_2 flame was shut off and a quick argon purge was used to remove the residual hot water vapor from the beam path. The 15 second radiance measurement (at 16 cm^{-1} resolution) is, therefore, an average radiance measurement as the sample cools, but H_2O free spectra are the result. As with the quartz, the spectral emittance as determined by closure is slightly elevated from non-zero in the transparent region for the sapphire, again indicating the possibility of an internal reflection effect.

Sample Class B

Silicon Nitride - Measurements of reflectance from a surface that reflects incident radiation anisotropically are shown in Fig. II.4.8. This silicon nitride surface had a "grain" pattern to it that was visible to the unaided eye. Clearly demonstrated is that rotational changes in the "grain" orientation with respect to the plane of incident, and collected IR radiation will result in grain influenced results. For each orientation and over all angles, however, the Christiansen dip is demonstrated at 1206 cm^{-1} , allowing for the surface temperature to be determined directly from a radiance measurement. Figure II.4.9 is of radiance measurements taken at each surface grain rotational orientation, overlaid with the theoretical black-body curve corresponding to the determined surface temperature. The temperatures vary between surface orientations because the sample was cooled, rotated and re-heated with the H_2 flame between each measurement. Figure II.4.9f of the spectral emittance for each orientation indicates agreement at all orientations. The spectra are "noisy" at high wavenumbers due to the lack of high energy radiation emitted by an 800 K surface.

Figure II.4.5. Spectral Emittance Calculated from IR Reflectance and Transmittance Measurements at 0.5 cm^{-1} Resolution for Optical Grade Fused Quartz at $\sim 900\text{K}$. a) Reflectance, b) Transmittance and c) Emittance $= 1 - \text{Reflectance} - \text{Transmittance}$. The Darkened Circles in (c) are from the Data of Myers et al., in Figure II.4.4d.

Figure II.4.6. Surface Temperature and Spectral Emittance of Optical Grade Fused Quartz Determined by Radiance Measurement and Zero Reflection/Transmission Feature. (0.5 cm⁻¹ spectral resolution) a) Radiance Overlayed with a 906K Theoretical Black-body Curve, b) Expanded View of (a) Showing Water Vapor Continuum on Top of Quartz Radiance Spectrum. Overlayed is the 906K Black-body Curve and a Water Vapor Spectrum and c) Emittance = Radiance/BB_{906K}.

Figure IL4.7. Comparison of Spectral Emittance for Optical Grade Fused Quartz at 900K Determined by Radiance Measurement and Zero Reflection/Transmission Feature to Closure by 1-Reflectance-Transmittance.

Figure II.4.8. Reflectivity at 800K for Five Rotational Orientations of Cercom Rough Si_3N_4 . a-e) Several Directional Integrated Components of Reflectivity and a'-e') Surface Ridge ("Grain") Influenced Total Hemispherical Reflectivity.

Figure II.4.9. Surface Temperature and Spectral Emittance Determination from Radiance and Zero Reflection/Transmission Feature for Five Rotational Orientations of Rough Si_3N_4 (Cercom). a-e) Radiance Overlaid with a Theoretical Black-body Curve Corresponding to the Surface Temperature and f) Comparison of Emittance = Radiance/BB(T_s) for Each Orientation. The Solid Lines Indicate the Visually Observed Surface Ridge Pattern ("Grain") of the Material.

Figure II.4.10 compares the spectral emittance obtained by the radiance measurement and Christiansen dip with an emittance calculated from the reflectance closure method by first averaging the hemispherical reflectance for the five surface grain orientations. Fairly good agreement is observed. Better agreement would be expected if the reflectance was taken for more rotational orientations of the surface, or if the surface was constantly rotated during reflectance measurement so that in-situ averaging would occur during the FT-IR collection. **As for Sample Class A, Class B materials allow for both closure and Christiansen dip techniques to be used to independently determine spectral emittance and temperature, thus assuring a high accuracy in the determinations.**

Sample Class C

For partially transparent materials that exhibit a large degree of internal multiple scattering, reflectance closure was prohibited due to radiation being directed out of the collection angle of our collection optics. If the material exhibits a Christiansen dip, however, as identified from a non-quantitative reflectance measurement, the surface temperature and spectral emittance could be determined spectroscopically.

Al₂O₃ Ceramic - Figures II.4.11 and II.4.12 demonstrate the determination for two samples of alumina ceramic (Al₂O₃) from two different manufacturers (Coors, and McDanel). For each sample the angle of specular reflection, although non-quantitative, exhibit a Christiansen dip. Measurements at all other collection angles also exhibits this zero reflection region, and measurements in the transmission hemisphere demonstrated IR opacity.

For the McDanel sample, a surface temperature of 1342 K was determined. A 0.005" diameter thermocouple that was pushed against the surface (not bonded) indicated 148 K lower. For the Coors sample determined to be 1415 K, the thermocouple indicated 174 K lower. One would expect the lower thermocouple indications due to the lack of sufficient surface contact and radiation loss to the room, and that the difference would be greater with hotter sample temperature.

Although only the Christiansen dip technique can be applied to these types of materials, a high degree of accuracy in the determined temperature and spectral emittance is still obtained. At the spectral region of zero reflectance and transmittance the accuracy in matching a theoretical black-body radiance to the measured surface radiance is within ± 5 K.

Figure II.4.13a compares the measured emittance for each of the Al₂O₃ samples. Differences may be due to thickness, pore size, grain size, etc., but each exhibit the shape of previously published data on Al₂O₃ (21) shown in Fig. II.4.13b.

Sample Class D

This class of surfaces applies to isotropically diffuse or specularly reflecting surfaces that do not exhibit a Christiansen dip. Most metallic surfaces would fall into this class.

Stainless Steel - Figure II.4.14 demonstrates the room temperature reflectivity from the top surface of a type 316 stainless steel pipe plug at three rotational orientations. The pipe plug had previously been exposed to oxidizing conditions. The reflectance and calculated room temperature emittance (Fig. II.4.15) at each orientation indicate that the surface reflects isotropically.

For elevated temperature measurements, the pipe plug was heated with two propane torches. Figure II.4.16 is a schematic showing the placement of the torches and thermocouples with respect to the surface of interest.

Reflectance measurements (Fig. II.4.17) were taken of the surface at two temperatures. The lower temperature case (758 K by surface bonded thermocouple) reflected incident radiation

Figure IL4.10. Spectral Emittance Determined by 1-Reflectance (average of five rotational orientations) Compared to Spectral Emittance Determined by Radiance Measurement (average of five rotational orientations) for Rough Si_3N_4 (Cercom) at 800K.

Figure II.4.11. Surface Temperature and Spectral Emittance of Coors' AL_2O_3 Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 1415K Theoretical Black-Body Curve, and c) Emittance = Radiance/ $\text{BB}_{1415\text{K}}$.

Figure II.4.12. Surface Temperature and Spectral Emittance of McDanel Al_2O_3 Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 1342K Theoretical Black-Body Curve, and c) Emittance = Radiance/BB_{1342K}.

Figure II.4.13. a) Spectral Emittance of Coors' Al_2O_3 at 1415K vs. McDanel's Al_2O_3 at 1342K and b) Spectral Emittance of Aluminum Oxide from Ref. 9.

Figure II.4.14. Comparison of Room Temperature Reflectivity for a Type 316 Stainless Steel Pipe Plug (oxidized surface) for Three Rotational Orientations of the Surface with Respect to the Plane of Incident and Collected IR Radiation. a-c) Several Directional Integrated Components of Reflectivity and a-c') Total Hemispherical Reflectivity.

Figure II.4.15. Comparison of Room Temperature Spectral Emittance Determined by 1-Reflectance for a Type 316 Stainless Steel Pipe Plug (oxidized surface) at Three Rotational Orientations of the Surface with Respect to the Plane of Incident and Collected Infrared Radiation (dashed line).

Figure IL4.16. Schematic of Heating Technique and Thermocouple Placement for a 1", Type 316 Stainless Steel Pipe Plug.

Figure IL4.17. Reflectivity for a Type 316 Stainless Steel Pipe Plug (oxidized surface) at Two Different Temperatures as Indicated by a 0.005" Thermocouple Bonded to the Surface. a-b) Several Directional Components of Reflectivity and c-d) Total Hemispherical Reflectivity.

into the hemisphere from $\theta = 15^\circ$ (specular) to $\theta = 45^\circ$, where as reflected radiation for the higher temperature case (1023 K by surface bonded thermocouple) was observed out to 60° . The spectral emittance from the reflectance closure for the lower temperature case and a radiance measurement are shown in Fig. II.4.18.

Also shown is the temperature spectrum calculated by Eq. 11 ($BB(T)_\nu = R_\nu / \epsilon_{\nu(1-p)_\nu}$) overlayed with the theoretical black-body radiance corresponding to the temperature indicated by the surface bonded thermocouple. The same analysis is shown in Fig. II.4.19 for the higher surface temperature case. For both low and high temperature, agreement is excellent between the temperature determined by reflectance closure and the surface bonded thermocouple above 2000 cm^{-1} . The reason for the deviation below 2000 cm^{-1} eludes us at this point. Figure II.4.20 compares the best fit temperatures to temperatures indicated by the internal and external thermocouples. As expected, the internally and externally placed thermocouples indicated a higher and lower temperature, respectively, than that indicated by both the surface bonded thermocouple and the temperature determined by reflectance closure.

Also demonstrated is that deviation on the order of $\pm 10 \text{ K}$ between the temperature determined by the reflectance closure and that indicated by the surface bonded thermocouple would be observable.

Sandblasted Aluminum - A surface of sandblasted type 6061 aluminum also exhibited Class D behavior. Before sandblasting the surface, the material reflected incident radiation anisotropically due to a cutting pattern etched on the surface. Figure II.4.21 indicates the isotropic reflection obtained after sandblasting and oxidizing the material at 785 K, as indicated by a surface bonded thermocouple. The melting point of aluminum is 933 K. The spectral emittance was calculated from an average of the two hemispherical reflectance spectra since a slight deviation still appeared between the two sample orientations. Figure II.4.22 shows the spectral emittance, a radiance measurement and the determined temperature from reflectance closure overlayed with the theoretical black-body radiance corresponding to the surface bonded thermocouple measurement. The agreement is excellent, and is shown to be sensitive to less than $\pm 10 \text{ K}$ deviations.

For this class of materials, only the closure method can be applied to determine the spectral emittance and temperature of the surface. Comparison to the temperature as indicated by surface bonded thermocouples demonstrated good agreement. The surface bonded thermocouples were not necessarily in agreement with the actual temperature of the surface, however. Given the many angles at which the reflected radiation is measured, we would expect slightly more error to be associated with diffuse reflecting surfaces than specular surfaces. Also, without verification of the determined emittance and temperature as we had for Class A and B materials by the Christiansen dip technique, the level of accuracy in the determination is expected to be slightly less than the previously described sample classes.

Sample Class E

For non-transmitting, anisotropically reflecting surfaces that do not exhibit a Christiansen dip, reflectance closure is obtainable if the surface is rotated to average the anisotropic reflectance into the collection optics. This technique was shown previously for rough Si_3N_4 with surface ridges. The Si_3N_4 , however, also exhibited a Christiansen dip, which made it a Class B material.

Aluminum - Figure II.4.23 compares two rotational orientations of the type 6061 aluminum at room temperature. As with the Si_3N_4 , a unidirectional surface grain was visually observable, and the reflectance measurements demonstrates the anisotropic nature of the surface. Rotating the sample to produce in-situ directional averaging would lead to reflectance closure, or the surface could be sandblasted to make it a Class D surface.

Figure II.4.18. Spectral Emittance and Surface Temperature Determination from Total Reflection and Radiance Measurements for a Type 316 Stainless Steel Pipe Plug. A Surface Bonded 0.005" Thermocouple Indicated a Temperature of 758K. a) Emittance = 1-Reflectance, b) Radiance Measurement of Surface and c) Calculated Temperature Spectrum (temperature = radiance/emittance) Overlayed with a Theoretical Black-body Temperature Curve Corresponding to the Thermocouple Temperature.

Figure II.4.19. Spectral Emittance and Surface Temperature Determination from Total Reflection and Radiance Measurements for a Type 316 Stainless Steel Pipe Plug. A Surface Bonded 0.005" Thermocouple Indicated a Temperature of 1023K. a) Emittance = 1-Reflectance, b) Radiance Measurement of Surface and c) Calculated Temperature Spectrum (temperature = radiance/emittance) Overlayed with a Theoretical Black-body Temperature Curve Corresponding to the Thermocouple Temperature.

Figure IL4.20. Comparison of Calculated Temperature Spectrum (temperature = radiance/emittance, where emittance = 1-reflection) to Observed Thermocouple Temperatures for a Type 316 Stainless Steel Pipe Plug at Two Temperatures.

Figure II.4.21. Reflectivity at 758K for a Sandblasted and Oxidized Surface of Type 6061 Aluminum. a) Several Directional Integrated Components of Reflectivity, b) Same as (a) after 90° Rotation of the Sample and c) Comparison of the Total Hemispherical Reflectivity for Each Rotational Position.

Figure IL4.22. Spectral Emittance and Surface Temperature Determination from Total Reflection and Radiance Measurements for Sandblasted Type 6061 Aluminum. a) Emittance = 1-Reflection, b) Radiance Measurement of Surface, c) Calculated Temperature Spectrum (temperature = radiance/emittance) Overlaid with Best-fit Theoretical Black-body Temperature Curve and d) Extent of Deviation for Theoretical Temperatures $\pm 10\text{K}$ from Best-fit Curve. A Surface Bonded 0.005" Thermocouple Indicated a Temperature of 758K.

Figure IL.4.23. Comparison of Room Temperature Reflectivity at Two Rotational Orientations for Type 6061 Aluminum. a-b) Several Directional Integrated Components of Reflectivity. a'-b') Surface Ridge ("Grain") Influenced Total Hemispherical Reflectivity.

Sample Class F

If a material is partially transmitting and diffuse reflecting, it will probably exhibit internal multiple scattering which has been shown to be detrimental to reflectance closure. If the material does not exhibit a Christiansen dip (which would make it a Class C material), only partial reflectance closure would be obtained to base the emittance and temperature determination. A very low accuracy in the determination is expected, but we did not encounter any technique validation materials in this class.

Achievements in Sample Heating, Temperature Uniformity and Measurement Speed - In an effort to elevate deposit samples to higher temperatures, improvements in the flame geometry of our oxygen/acetylene torch heating system were investigated on a 0.188" thick slab of sintered Al_2O_3 ceramic, which was shown to exhibit a Christiansen Dip at 995 cm^{-1} .

Figure II.4.24 demonstrates the high surface temperature achieved when the Al_2O_3 slab is directly heated with the flame on the surface being measured. Overlayed on the Al_2O_3 radiance spectrum is the theoretical black-body radiance spectrum that matches the Al_2O_3 radiance at the Christiansen Dip region (emissivity = 1.0), thus determining the surface temperature to be 2210 K. Also overlayed is the radiance of the isolated combustion products of the flame (CO_2 and H_2O). The amplitude of the gas species that cross the optical path are much less than that of the sample, and contribute only in well defined spectral regions. The small CO_2 contribution in the Al_2O_3 spectrum could be subtracted out. Thus, with the proper positioning of the front flame with respect to the measuring point, high temperatures can be achieved with a minimum of interference from the combustion products. Samples can of course, be only back-heated, which results in no radiance contribution from hot CO_2 , but the maximum measured surface temperature obtainable will be more dependent on the thickness of the sample.

By employing two $\text{O}_2/\text{C}_2\text{H}_2$ torches to back-heat the Al_2O_3 sample, a maximum surface temperature near 2000 K was obtained. To study the uniformity of heating with the torches, the temperature across a surface of Al_2O_3 was monitored by incrementally translating the sample and the two $\text{O}_2/\text{C}_2\text{H}_2$ torches that were back heating the sample across the FT-IR collection optics. The temperature was determined from the radiance amplitude at the Christiansen dip. Figure II.4.25 plots the measured surface temperature with respect to position on the surface, which was 17 mm across. The focal spot size measurement area was ~ 3 mm in diameter. The measurements taken at positions -8 mm and +8 mm were considered to be partially off the sample surface, since high levels of hot CO_2 were observed in the spectrum. No hot CO_2 was observed when the focal spot was completely on the surface (-7 mm to +7 mm). The plot indicates that except for near the edges, the surface is uniform to $\pm 25\text{ K}$ when near 2000 K. The difference on each side of the center point is attributed to slightly different flame conditions of the two torches. On each side of the center point, however, are 3 mm to 4 mm diameter regions that exhibit temperature uniformity to $\pm 5\text{ K}$. To have established this degree of temperature uniformity over an area larger than the spectroscopic focal area is extremely good considering: 1) the non-optimized heating geometry used, and 2) that sintered Al_2O_3 is a worst-case sample due to its porosity and low thermal conductivity.

Maximum measurement speed is demonstrated in Figure II.4.26. The figure presents single scan radiance measurements from an Al_2O_3 surface with the FT-IR spectrometer set to measure at a rate of 0.11 sec/scan. The Christiansen dip technique was employed to determine the surface temperature of the sample as it rapidly cooled from a stable high temperature condition

(time = 0, temperature = 2210 K) after the torch was removed from the sample. The surface temperature was measured to decrease 88 K in the first 0.11 sec of cooling. These spectra demonstrate that the FT-IR spectrometer can be used to measure extremely rapid changes in temperature and emissivity, which may be useful for possible in-situ applications in the future.

Figure II.4.24. Comparison of Radiance of Al_2O_3 at 2210 K when Heated from the Front with an $\text{O}_2/\text{C}_2\text{H}_2$ Torch with Radiance of Combustion Products from Torch when Sample is Removed.

Figure II.4.25. Measurement of Surface Temperature for Al_2O_3 as the Surface is Incrementally Translated across the FT-IR Collection Optics.

Figure II.4.26. Radiance Spectra from Al_2O_3 (McDanel Refractory Co.) with Theoretical Black-body Curves Corresponding to the Surface Temperature. Each Spectrum is a Single Scan with the FT-IR Spectrometer set to Collect Data at a Rate of 0.11 sec/scan. a) Time = 0 has the Surface being Heated with a $\text{O}_2/\text{C}_2\text{H}_2$ Flame; b-i) Flame Removed from Sample to Measure Radiance as the Sample Rapidly Cools.

Figure II.4.27 shows the spectral emittance calculated from the rapid radiance measurements and the surface temperature ($\epsilon_\nu = R_\nu / BB(T)_\nu$), and indicates that in the high absorbance region of the Al_2O_3 (the Christiansen dip region) the emittance is constant with temperature, but changes in emittance are observed with temperature in other spectral regions. This is in agreement with Fig. II.4.13b, which shows the array of data for Al_2O_3 , compiled in Ref. 21. There are differences between results obtained by different research workers, but when only one level of purity, and one temperature are compared, much of the scatter goes away (21). Our example shows how rapidly emittance data can be obtained as a function of temperature.

Figure II.4.27. Spectral Emittance Calculated from Radiance Measurements and Determined Surface Temperature from Figure 2.3. ($\epsilon = \text{Radiance}/B_{\text{surface}}$ temperature).

III. PROJECT RESULTS FOR ASH AND SLAG

III.1. Deposit Sample Acquisition

AFR acquired five slag samples from the Babcock & Wilcox Company and three ash samples from Stanford University. To compare slags formed in different combustion units, AFR also acquired a slag sample from Brigham Young University, (BYU), which was formed from coal similar to that fired at Babcock & Wilcox Company. The BYU slag had attached to it, a piece of furnace wall refractory which was also measured for emittance. All the acquired samples are described in Table 3.

III.2. Deposit Sample Characterization

Absorbance spectra of ground samples for the slag and ash acquired from Babcock & Wilcox and Stanford University suspended in KBr and CsI media are presented in Fig. III.2.1 to III.2.8. The inorganic components of these materials produces spectra with similar absorbance characteristics at low wavenumbers. The broad band slope in these spectra are characteristic of light scattering by the fine particulates. From such spectra, work was performed to measure the optical constants n_p and k_p for ash and slag deposits. AFR has developed a technique using the absorption measurements that eliminate the inaccuracies inherent in reflection techniques when applied to inhomogeneous materials such as ash or coal. The objective of the procedure as originally developed was to determine values of n_p and k_p which were consistent with extinction measurements using KBr and CsI pellets (an extension of the method of Brewster and Kunitomo (16)) and also consistent with the emissivity measurements. The technique has previously been described (22,23).

Figure III.2.9 compare measurements of the optical constants for the sintered sample #1 and the powdery ash #7. These will be used as input for model predictions of emissivity for ash and slag.

Elemental x-ray analysis of the deposits resulted in only qualitative analysis at this time, due to the lack of instrument calibration for high levels of such components. Qualitative analysis does show the main constituents to be silica, calcia, and iron oxides, as expected. The normalized concentrations for the elements determined by our analyzer, presented in their oxide form, are shown in Table 4. Slight variations are observed between the slag samples removed from the Basic Combustion Test Unit at B&W, which originated from the same coal. Large variations are observed in the powdery ash received from Stanford University, which originate from lignite, bituminous, and subbituminous coals. X-ray analysis were not performed on samples #3 and #4 because these were supplied to AFR in such small quantities that laboratory emittance measurements could not be made.

III.3. Measurement of Radiative Properties of Deposit Samples

All samples were heated with either a propane or oxy/acetylene flame; and most had a 0.005" diameter type K thermocouple bonded to the surface as close to the measurement spot as possible. Surfaces were measured. All surfaces were measured as received with no smoothing or polishing. The powdery ash samples were pressed into wafers to allow for the surface measurements. All of the measured samples were thick enough to be opaque to the incident infrared radiation from the spectrometer's source ($\tau_p = 0$). Based on the surface measurements, each sample was related to the classification scheme developed during technique validation.

One experimental difficulty that was identified during these measurements was that some of the samples exhibited extremely low amounts of intensity for the angular reflection measurements. This may be attributed to a high degree of multiple scattering effects, which was shown in the technique validation section to direct much of the incident IR energy out of the acceptance angle of the collection optics. The low signal made it difficult to ensure

TABLE 3
SLAG AND ASH SAMPLES

SAMPLE NO.	SLAG OR ASH DESCRIPTOR	ACQUIRED FROM	COAL	FIRE AT	PHYSICAL DESCRIPTION
1	Slag from refractory back wall of BCTU*	B & W	Illinois No. 6 (bituminous)	B & W	Sintered Deposit
2	Slag from top of slagging panel in BCTU	B & W	Illinois No. 6 (Bituminous)	B & W	Fused Deposit
3	Slag from Tube No. 2 of slagging panel in BCTU	B & W	Illinois No. 6 (Bituminous)	B & W	Dusty Deposits
4	Slag from Tube No. 4 of slagging panel in BCTU	B & W	Illinois No. 6 (Bituminous)	B & W	Dusty Deposits
5	One-time molten pool of slag from inside BCTU	B & W	Illinois No. 6 (Bituminous)	B & W	Fused Deposit
6	Eagle Butte Ash	Stanford University	Eagle Butte (Subbituminous)	Paynee Station Brush, Colorado	Powdery Ash
7	San Miguel Ash	Stanford University	San Miguel (Texas Lignite)	San Miguel Station San Miguel, TX	Powdery Ash
8	Illinois No. 6 Ash	Stanford University	Illinois No. 6 (Bituminous)	Labadie Station	Powdery Ash
9	BYU Furnace Wall Refractory	BYU	-----	BYU	Hard Alumina & Chromium Based Material
10	BYU Slag	BYU	Illinois No. 6 (Bituminous)	BYU	Fused Deposit

* BCTU: Basic Combustion Test Unit at B & W

Figure III.2.1. Measured Absorbance Spectra for Sample #1, Babcock and Wilcox Sintered Slag Deposit (back wall) in a) KBr and b) CsI.

Figure III.2.2. Measured Absorbance Spectra for Sample #2, Babcock and Wilcox Fused Slag Deposit (top of panel) in a) KBr and b) CsI.

Figure III.2.3. Measured Absorbance Spectra for Sample #3, Babcock and Wilcox Dusty Slag Deposit (tube #2) in a) KBr and b) CsI.

Figure III.2.4. Measured Absorbance Spectra for Sample #4, Babcock and Wilcox Dusty Slag Deposit (tube #4) in a) KBr and b) CsI.

Figure III.2.5. Measured Absorbance Spectra for Sample #5, Babcock and Wilcox One-Time Molten Pool of Slag in a) KBr and b) CsI.

Figure III.2.6. Measured Absorbance Spectra for Sample #6, Eagle Butte Ash in a) KBr and b) CsI.

Figure III.2.7. Measured Absorbance Spectra for Sample #7, San Miguel Ash in a) KBr and b) CsI.

Figure III.2.8. Measured Absorbance Spectra for Sample #8, Illinois No. 6 Ash in a) KBr and b) CsI.

Figure III.2.9. Measured Real and Imaginary Parts of the Index of Refraction. $N_v = n_v + ik_v$, for a) Sintered Slag Sample #1 and b) Powdery Ash #7.

TABLE 4

COMPOSITIONAL X-RAY ANALYSIS FOR ASH AND SLAG DEPOSIT SAMPLES

Inorganic Component	Sample #1 Sintered Deposit (Ill No. 6, Bit. Coal)	Sample #2 Fused Deposit (Ill No. 6, Bit. Coal)	Sample #5 Fused Deposit (Ill No. 6, Bit. Coal)	Sample #6 Powdery Ash (Eagle Butte, Subbit. Coal)	Sample #7 Powdery Ash (Texas Lignite)	Sample #8 Powdery Ash (Ill No. 6, Bit. Coal)
Na ₂ O	0	0.05	2.76	0.07	2.11	0.33
MgO	0	0	1.47	3.28	0	0
Al ₂ O ₃	10.96	11.12	18.16	12.80	17.11	11.37
SiO ₂	52.17	59.28	56.21	23.61	70.63	47.35
K ₂ O	2.23	2.04	1.47	0.59	1.55	2.02
CaO	7.22	4.96	4.13	37.77	4.32	4.58
TiO ₂	1.08	1.04	1.01	1.65	1.05	1.04
SO ₃	2.56	0.09	0.12	7.08	0.94	9.20
Fe ₂ O ₃	23.71	20.97	14.68	13.00	2.53	23.91

precise alignment of the surface with respect to the incident and collected IR energy. For some of the samples, the acceptance angle of the collection optics was increased to produce an acceptable reflection signal.

If precise alignment is not known, or if the acceptance angle is increased our quantitative analysis method, as described in the technique validation section, for the total hemispherical reflection becomes invalid.

These conditions are acceptable if the surface exhibits a Christiansen Dip, since the total hemispherical reflectivity is not needed for the temperature and emittance determination.

Some samples did not allow for reflectance closure and did not exhibit a Christiansen Dip. In our sample classification scheme, these samples would be considered Class F. It was observed, however, that angular reflection measurements, although non-quantitative, did indicate fairly constant gray-body emittance over large spectral regions. That is, if each angular reflectivity measurement remains constant over a large spectral region (i.e., no slope), the total reflection will also be constant over a large spectral region. Closure analysis then defines that the emittance in this spectral region also must remain constant (i.e., no slope, constant gray-body). The spectral emittance can be calculated from the radiance measurement until constant gray-body emittance was indicated in the appropriate spectral region. The surface temperature arrived at by this method was in good agreement with the temperature indicated by the thermocouple that was bonded to the surface of each sample.

Fused Deposits

Sample No. 5: One-time Molten Pool of Slag from Inside BCTU - This sample arrived at AFR as 4" to 5" sized pieces that were chiseled out of the BCTU from a solidified pool of once molten slag. The top surface and two internal surfaces were measured for emittance.

No. 5 Top Surface (flat): Sample Class D - Figure III.3.1 shows quantitative reflectivity measurement from this flat purple surface at an elevated temperature. A surface bonded thermocouple indicated a temperature of 964 K. Figure III.3.2 follows through the reflectance closure analysis, which resulted in a spectroscopically determined surface temperature of 945 K, which is within 20 K of the thermocouple indication. Figure III.3.3 compares the spectral emittance from the measured hemispherical reflectance with that calculated from the radiance measurement (Fig. III.3.2b) and the spectroscopically determined surface temperature. Good agreement is demonstrated.

The same analysis is shown in Fig. III.3.4 for a different measurement spot of the top surface that was heated to a higher temperature.

Figure III.3.4a shows the spectral emittance determined by reflectance closure ($\epsilon = 1 - \text{reflectance}$). Figure III.3.4b shows the radiance measurement; and Figs. III.3.4c and III.3.4d indicate the determined surface temperature from these measurements (surface temperature = Radiance/ ϵ) to be 1630 K $\pm$ 10 K. Figure III.3.5a compares the closure emittance to the emittance calculated from the radiance measurement and the determined surface temperature ($\epsilon = 1 - \text{reflectance}$ vs. $\epsilon = \text{Radiance}/BB_{1630\text{ K}}$), and good agreement is demonstrated. Figure III.3.5b allows for comparison to the spectral emittance determined at 945 K. There is apparently negligible changes in the spectral emittance for this sample over this temperature range. Slight variations observed below 1500 cm^{-1} , which is the characteristic region of infrared band absorption for mineral species found in ash and slag, could be due to either chemical changes upon heating to the higher temperature or variations in composition at different measurement spots.

No. 5 Inside Surface (smooth): Sample Class B - Fracturing the solidified slag to obtain an internal surface resulted in "wavy" surfaces that reflect anisotropically. The surfaces did exhibit a Christiansen Dip, however. Figure III.3.6 follows through the surface temperature

Figure III.3.1. Reflectivity of Slag from Babcock and Wilcox's Basic Combustion Test Unit, Sample #5, Top Surface. a) Several Directional Integrated Components of Reflectivity, and b) Total Hemispherical Reflectivity.

Figure III.3.2. Spectral Emittance and Surface Temperature from Total Reflection and Radiance Measurements for Slag from Babcock and Wilcox's Basic Combustion Test Unit, Sample #5, Top Surface. a) Emittance = 1-Reflection, b) Radiance Measurement, c) Calculated Temperature Spectrum (temperature = radiance/emittance) Overlaid with Best Fit Theoretical Black-body Temperature Curve and d) Extent of Deviation $\pm 20\text{K}$ from Best Fit Curve. A Thermocouple Bonded to the Surface Indicated 964K.

Figure III.3.3. Comparison of Spectral Emittance Calculated from $\epsilon = 1\text{-Reflection}$ vs. $\epsilon = \text{Radiance}/\text{BB}_{945\text{K}}$ for Slag from Babcock and Wilcox BCTU, Sample #5, Top Surface.

Figure III.3.4. Spectral Emittance and Surface Temperature from Total Reflection and Radiance Measurements for Slag from Babcock & Wilcox's Basic Combustion Test Unit, Sample #5, Top Surface. a) Emittance = 1-Reflection, b) Radiance Measurement, c) Calculated Temperature Spectrum (temperature = radiance/emittance) Overlaid with Best Fit Theoretical Black-body Temperature Curve, and d) Extent of Deviation $\pm 20\text{ K}$ from Best Fit Curve.

Figure III.3.5. Comparison of Spectral Emittance Calculated from $\epsilon = 1\text{-Reflectance}$ vs. $\epsilon = \text{Radiance/BB}$ for Fused Slag (Sample #5, Top Surface) at: a) 1630 K and b) 945 K.

Figure III.3.6. Surface Temperature and Spectral Emittance from Radiance Measurement and Zero Reflection/Transmission Feature for Slag from Babcock and Wilcox's Basic Combustion Test Unit, Sample #5, Internal Smooth Surface. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 950K Theoretical Black-Body Curve, c) Emittance = Radiance/BB_{950K} and d) Sensitivity of Emittance Calculation to $\pm 1\text{K}$ where $\epsilon = 1$. A Thermocouple Bonded to the Surface Indicated a Temperature of 973K.

and spectral emittance determination from the Christiansen Dip analysis. The spectroscopically determined surface temperature was within 25 K of that indicated by the surface bonded thermocouple.

Later in the program a smooth thin slice was obtained that did not exhibit the anisotropic reflection of the "wavy" surface. Figure III.3.7 presents the measured hemispherical reflectivity and spectral emittance measured at room temperature. The spectral emittance is again similar over a wide temperature range (Fig. III.3.7c).

No. 5 Inside Surface (rough): Sample Class B - The spectral emittance as determined by the Christiansen Dip method (Fig. III.3.8) was similar, but slightly higher than that of the smooth, and hence, slightly more reflective inside surface. The spectroscopically determined surface temperature was within 30 K of that indicated by the surface bonded thermocouple.

Sample No. 2: Fused Deposit from BCTu; Sample Class F - This material was not as smooth surfaced as fused sample No. 5. The surface was very rough with swirl patterns from what is assumed to be due to movements when in the molten state. Because of the surface topology, quantitative reflection measurements were not possible. The qualitative measurements shown in Fig. III.3.9a do not indicate a Christiansen dip, but do indicate constant gray-body emittance above 2500 cm^{-1} . Figure III.3.9c shows the emittance calculated from the radiance measurement (Fig. III.3.9b) with 20 K shifts in temperature, with 787 K being the determined surface temperature. The surface bonded thermocouple indicated a temperature that was 46 K higher.

Sample No. 10: Fused Deposit from BYU; Class F - This material was similar to sample No. 2 that was described above. Qualitative reflection measurements indicated constant gray-body emittance above 2500 cm^{-1} . Figure III.3.10 follows through the emittance determination. The spectroscopically determined surface temperature 944 K was 17 K higher than the surface bonded thermocouple.

Sintered Deposits

Sample No. 1: Sintered Deposit from BCTU; Sample Class F - This sample was very brittle and irregular shaped on the surface. Precise alignment was impossible for this surface and the collection angle of the optics was increased to produce a detectable reflection signal. As Fig. III.3.11a shows, less than 0.10% energy was collected at the presumed specular position. However, constant gray-body emittance is indicated above 4000 cm^{-1} by the flatness of the reflectance in both the 15° and 45° measurements.

The radiance measurement of Fig. III.3.11b was divided by theoretical black-body temperature curves until a constant gray-body feature was demonstrated above 4000 cm^{-1} . Figure III.3.11c shows three emittance calculations with 20 K shifts in temperature. The spectra are "noisy" at high wavenumbers due to the lack of high energy radiation emitted by an 800 K surface. Clearly, a temperature of 793 K produces a constant (flat) emittance above 4000 cm^{-1} .

The surface bonded thermocouple indicated a temperature that gradually increased from 785 K to 801 K during the radiance measurement. The average thermocouple temperature of 793 K is the same as that which produces the constant gray-body feature above 4000 cm^{-1} . Figure III.3.11d isolates the emittance determined at this temperature. Also worth noting is that all of the spectral features in the reflectance measurements are present in the emittance spectrum, even though they were produced from completely separate measurements.

Powdery Ash Deposits

Sample No. 7: San Miguel Ash; Sample Class A - Figure III.3.12a shows the spectral emittance of a pressed wafer of the powdery ash calculated from reflectance closure ($\epsilon = 1 -$

Figure III.3.7. Room Temperature Spectral Emittance Determination for Slag Sample #5, Internal Smooth Surface. a) Hemispherical Reflectance, b) Spectral Emittance and c) Comparison to Emittance Determined at 950K.

Figure III.3.8. Surface Temperature and Spectral Emittance from Radiance Measurement and Zero Reflection/Transmission Feature for Slag from Babcock and Wilcox's Basic Combustion Test Unit, Sample #5, Internal Rough Surface. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 1111K Theoretical Black-Body Curve, c) Emittance = Radiance/BB_{1111K} and d) Sensitivity of Emittance Calculation to ± 1 K where $\epsilon = 1$.

Figure III.3.9. Spectral Emittance and Surface Temperature Determination for Babcock and Wilcox Fused Slag, Sample #2. a) Reflection at the 15° and 45° Angle, b) Radiance Measurement, c) Spectral Emittance Calculated at Three Temperatures (767K, 787K, 807K) and d) Spectral Emittance at 787K. A Surface Bonded Thermocouple Indicated a Temperature of 833K.

Figure III.3.10. Spectral Emittance and Surface Temperature Determination for BYU Gray Fused Slag, Sample #10.
a) Reflection at the Specular Angle, b) Radiance Measurement, c) Spectral Emittance Calculated at Three Temperatures (924K, 944K, 964K) and d) Spectral Emittance at 944K. A Surface Bonded Thermocouple Indicated a Temperature of 927K.

Figure III.3.11. Spectral Emittance and Surface Temperature Determination for Babcock and Wilcox Sintered Slag, Sample #1. a) Reflection at the 15° and 45° Angle, b) Radiance Measurement, c) Spectral Emittance Calculated at Three Temperatures (773K, 793K, 813K) and d) Spectral Emittance at 793K. A Surface Bonded Thermocouple Indicated a Temperature of 793K.

Figure III.3.12. Spectral Emittance and Surface Temperature from Total Reflectance and Radiance Measurement for a Pressed Wafer of San Miguel Powdery Ash (Sample #7). A Christiansen Dip is also Observed. a) Emittance = 1-Reflectance, b) Radiance Measurement Overlayed with 1242 K Theoretical Black-body Curve, c) Surface Temperature = Radiance/ ϵ_1 -reflectance Overlayed with BB = 1242 K, and d) ϵ_1 -reflectance Compared to $\epsilon = \text{Radiance} / \text{BB}_{1242\text{K}}$.

reflectance). Reflected IR radiation was detected from the 15° specular angle out to 75°. The 2 mm wafer was opaque to the incident IR radiation ($\tau_p = 0$).

The emittance spectrum indicates that both the reflectance closure analysis and the Christiansen dip analysis can be applied to determine the surface temperature. Figure III.3.12b is the radiance measurement of the surface overlayed with a theoretical black-body spectrum which matches the ash wafer radiance measurement at the Christiansen dip region. A temperature of 1242 K was used to calculate the black-body radiance. In Fig. III.3.12c, the surface temperature is independently determined from the radiance measurement and the spectral emittance calculated from 1-reflectance. The best fit black-body radiance corresponds to 1242 K, the same as the Christiansen dip technique. Figure III.3.12d compares the closure emittance to the emittance calculated from the radiance measurement and the determined surface temperature ($\epsilon = 1 - \text{reflectance}$ vs $\epsilon = \text{Radiance}/\text{BB}_{1242\text{ K}}$), and good agreement is demonstrated.

Furnace Wall Refractory

Sample No. 9: Furnace Wall Refractory from BYU; Sample Class C - Qualitative measurements indicated a Christiansen Dip region. Figure III.3.13a shows a reflection measurement of the sample at ~ 1000 K as indicated by the surface bonded thermocouple. Two regions where $\epsilon_p = 1.0$ are indicated at ~ 1250 cm^{-1} and ~ 950 cm^{-1} . Radiance measurements taken at three different surface temperatures are shown in Figs. III.3.13b to III.3.13d. These are overlayed with the theoretical black-body curve corresponding to the temperature defined by the Christiansen Dip regions. Also noted is the surface bonded thermocouple temperature for each case. Figure III.3.14 compares the calculated emittance for each case. The spectral emittance is not observed to greatly change through this temperature range. The spectra show that the emittance increases only slightly as temperature is increased. Notable is that the $\epsilon_p = 1.0$ region at ~ 1250 cm^{-1} is maintained at all three temperatures, but $\epsilon_p = 1.0$ is not maintained for the 950 cm^{-1} region as temperature is lowered.

This effect was confirmed by measuring a qualitative reflectance of the surface at room temperature. The 950 cm^{-1} region did not indicate zero reflectance as it did when it was hot.

III.4. Analysis of Measurements on Deposit Samples

Fused Deposits - Figure III.4.1 compares the determined spectral emittance for all of the fused slags acquired ranging in temperature from 300 K to 1630 K. All exhibit a high spectral emittance (≥ 0.9). The variations observed below 1500 cm^{-1} again indicates the sensitivity of the technique to discrete changes in mineral species for the samples. Shaded in the figure are the interference regions of the combustion products (CO_2 and H_2O) of the flames used to heat the samples. In sample #2, at 787 K, the region of the spectrum becomes noisy above 5000 cm^{-1} because of the lack of available energy radiated by the sample in this region at this low temperature.

Sintered or Powdery Deposits - Large excursions in spectral emittance occur for the sintered and powdery ash deposits, as shown in Fig. III.3.11 and III.3.12. This is attributed to the differences in surface morphology (texture) between the fused and sintered or powdery states. The powdery ash and, to a lesser degree, the sintered samples consists of small individual mineral particles that are weakly held together whereas the fused deposits have solidified from a molten state. The individual particles of the powdery and sintered deposits increase the scattering efficiency of these materials, which will cause a wavelength dependent drop in emittance. To further substantiate the effect of texture on radiative property measurements, reflectance and transmittance measurements were performed on pressed pellets of KBr, which has a low absorption coefficient in the IR and is transparent when it is in homogeneous pellet form (i.e., the form of a KBr optical window). The data are presented in Fig. III.4.2. Under 10 tons of pressure, the reflectance is about 7%, while the transmittance is

Figure III.3.13. Surface Temperature Determined by Christiansen Dip Analysis for BYU Furnace Wall Refractory Sample #9, at Three Temperatures. a) Reflection at the Specular Angle at the Hottest Temperature, b-d) Radiance Measurements Overlayed with the Appropriate Theoretical Black-Body Curve Corresponding the the Surface Temperature (also shown is the surface bonded thermocouple temperature for each case).

Figure III.3.14. Spectral Emittance Calculated from the Radiance Measurements and Corresponding Black-Body Temperature Curve from Fig. III.3-13b-d for BYU Furnace Wall Refractory Sample #9, at Three Temperatures. a) Spectral Emittance at 703K, b) Spectral Emittance at 874K, c) Spectral Emittance at 1039K and d) Comparison of the Spectral Emittance at each Temperature.

Figure III.4.1. Comparison of Measured Spectral Emittance for Several Fused Slag Samples Over a Wide Temperature Range.

Figure III.4.2. Pressure Influence on a) Reflectance and b) Transmittance for Pressed Wafers (1mm thick) of KBr Powder at 25°C.

90%. The KBr pellet can retain internal cracks and surfaces if the pressure applied is insufficient to fuse the material. At one-half ton pressure, the reflectance is as high as 50% and the transmittance reduced to 30%. At only 170 lbs of pressure, the reflectance is as high as 70% with the transmittance near zero. In principal, the reflectance and transmittance should add to 100% for this non-absorbing material; but because of the pellet's diffuse scattering, the reflected or transmitted radiation can emerge from the surface so far from the entrance point that it is not recovered by our collection optics which are directed at the entrance point. The influence of sample texture is, however, clearly demonstrated.

To extend this analysis to ash and slag deposits, Fig. III.4.3a compares the spectral emittance of the sintered deposit to the same material after grinding into smaller particles and pressing into a wafer, and after melting the material. Fusing the sintered deposit results in a spectral emittance similar to those shown in Fig. III.4.1. In the molten or liquid state, the spectral emittance is apparently only slightly higher than the fused state, but does exhibit a Christiansen dip where $\epsilon_{\nu} = 1.0$. The hot CO₂ band at $\sim 4.5 \mu\text{m}$ is produced by the torch that is directly heating the measured spot. The melting point of the material was determined to be $\sim 1400 \text{ K}$. The individual particles of the surface of the original sintered deposit increase the scattering efficiency of the material, which will cause a wavelength dependent drop in emittance. By grinding the material to smaller particulates, the scattering efficiency is further increased and hence, results in a lower emittance. Figure III.4.3b also demonstrates the change in spectral emittance for fine particulates of powdery ash (sample no. 7) after fusing the material.

Analysis of Growing Deposits - The influence that particle-like deposits will have on the emittance of a surface was readily demonstrated. The measurement technique was applied to show the change in spectral emittance (and hence, in heat absorption rate) for a surface as ash deposit thickness is increased. Measurements were performed on a heavily oxidized stainless steel surface after subjecting the surface to impaction with the particle and fume stream from the combustion of pulverized Illinois No. 6 bituminous coal. The steel surface temperature, as measured with a 0.005" diameter thermocouple that was bonded to the surface, was held at $1000^{\circ}\text{F} \pm 30^{\circ}\text{F}$ during the ash deposition, and at $980^{\circ}\text{F} \pm 10^{\circ}\text{F}$ during the reflectivity measurements. These temperatures are in the range typical of a boiler wall or tube surface during operation.

Figure III.4.4 demonstrates the change in the spectral emittance (emittance = $1 - \text{reflectance}$) of the oxidized steel surface as it is increasingly coated with dusty ash deposit. Below 1500 cm^{-1} , where the strong absorption bands for coal ash in general, are located, the emittance continually increases as more material is deposited. Above 1500 cm^{-1} , there is initially a slight rise in emittance and then a continual decrease in emittance as the ash coating thickens and increases the reflectivity in this spectral region. The thickness of the most heavy deposition was measured by SEM photomicrographs to be $< 50 \mu\text{m}$ thick, but is already approaching the spectral shape for emittance of the much thicker pressed wafer of dusty fly ash shown in Fig. III.4.3b.

Attenuation Characteristics of Molten Slag - Fused deposits upon coating a surface will rapidly show spectral emittance characteristics of the fused material. Transmittance measurements through several cross-sectionally thin samples of three of the deposits in their fused state were performed. These samples were fabricated by melting the deposits on top of a 1/4" ID ceramic tube and then puffing the molten bead into a thin walled bubble that was allowed it to solidify. Breaking several of these resulted in thin slabs of fused slag which were measured with our SEM for thickness and by FT-IR transmittance spectroscopy for opaqueness. The percent transmittance at 6500 cm^{-1} for the samples are shown in Fig. III.4.5. Also shown are theoretical curves for attenuation of radiation by a medium as calculated by

$$I/I_0 = e^{-\alpha d} \quad (13)$$

Figure III.4.3. Measured Spectral Emittance for a) Sintered Slag Deposit (sample#1) Compared to the Material After Grinding and Pressing into a Wafer; and After Thermally Fusing the Material and b) Powdery Ash (sample #7) Compared to the Emittance After Thermally Fusing the Material.

Figure III.4.4. Spectral Emittance by Measured Hemispherical Reflectance (emittance = 1-reflectance) for a) an Oxidized Stainless Steel Surface, and b-d) the Surface as Increasingly more Dusty Ash is Deposited on the Surface. The Surface Temperature for Ash Deposition was Held at $1000^{\circ}\text{F} \pm 30^{\circ}\text{F}$; and for Measurements at $980^{\circ}\text{F} \pm 10^{\circ}\text{F}$.

Figure III.4.5. Theoretical Attenuation vs. Observed Attenuation for Fused Slags.
a) Sample No. 1 and No. 5 from the Firing of Illinois No. 6 Coal (bituminous) and
b) Sample No. 7 from the Firing of San Miguel Texas Lignite.

where t is the medium's thickness, I_0 is the irradiance when $t = 0$, and the absorption coefficient α is

$$\alpha = 4 \pi k / \lambda \quad (14)$$

where λ is wavelength and k is the imaginary part of the complex index of refraction. Plots of k for samples #1 and #7 were previously shown in Fig. III.2.9. 6500 cm^{-1} was chosen for the analysis since it is a wavelength of high transmittivity when compared to low wavenumbers where the mineral species absorb.

Agreement between theoretical and observed attenuation is good and indicates that for these fused samples opaqueness to infrared radiation is achieved within $200 \mu\text{m}$ deposit thickness.

III.5. Modeling of Radiative Properties of Deposit Samples

The optical properties of a sample depend mainly on the optical constants, n and k , of the constituent material, and on its state of aggregation and surface condition. For example, from the emittance of the slag deposit in various states shown in Fig. III.4.3, differences can clearly be observed between the homogeneous material in the liquid and fused states, the heterogeneous (i.e. containing voids) ground and pressed sample, and the heterogeneous sintered sample. The purpose of this task was to incorporate the optical constants of the slag into various models, and to compare predictions of the models with the observed emittances. Three models have been considered, one for a homogeneous slab, and two for samples of distributed matter.

Homogeneous Slab Model

The emittance, ϵ_ν , of a smooth surfaced, homogeneous slab at normal emergence is given by Eq. 15 (15)

$$\epsilon_\nu = 1 - \frac{[(n_\nu - 1)^2 + k_\nu^2]}{[(n_\nu + 1)^2 + k_\nu^2]} \quad (15)$$

Predictions of this model give reasonable agreement with the measured emittance of the fused sample (Fig. III.5.1), although a calculation using a void fraction (see discussion below) of about 0.15 would give better agreement.

There is another situation for which Eq. 15 applies. It is for a slab made by compressing or sintering very fine particles, so that over one wavelength the radiation samples many particles and voids (15). In this case an effective dielectric constant is estimated, and used to calculate n and k in Eq. 15. The effective dielectric constant depends on the void fraction, and was calculated using the Maxwell-Garnett model (15). The void fraction of the ground and pressed sample was measured, and the emittance was calculated using this value and the measured n and k (Fig. III.5.2). The emittance spectrum calculated from this model showed very poor agreement with the one measured for the ground and pressed sample of Fig. III.4.3. It is concluded that the ground sample does not fulfill the requirements of the model; i.e. the particle sizes are too large. The next two models we describe are more appropriate for this type of sample.

Two-Stream Model

A simple, analytical model has been used to calculate the emissivity of an opaque sample consisting of a collection of spheres (24). This approximate two stream model is much simpler to employ than exact 3-D models and is reasonably accurate. In this model,

$$\epsilon_\nu = 1 - R_\nu \quad (16)$$

Figure III.5.1. Measured Emittance Compared to Prediction for a Fused Surface of Sintered Sample #1.

Figure III.5.2. Absorbance Calculated for a Collection of Micro Particles of Slag, at a Void Fraction of 0.5. This Curve does not Fit the Measured Ground and Pressed Wafer Spectrum of Fig. III.4.3.

where R is the reflectivity of the sample, given by

$$R = \frac{(\sqrt{(1-\omega_o)g}) - \sqrt{(1-\omega_o)}}{(\sqrt{(1-\omega_o)g}) + \sqrt{(1-\omega_o)}} \quad (17)$$

where g is the asymmetry parameter, and

$$\omega_o = Q_{sca}/Q_{ext} . \quad (18)$$

The parameters Q_{sca} and Q_{ext} are the efficiency factors for scattering and extinction, respectively, and all quantities are spectral quantities.

In our first calculation of ϵ using Eqs. 16 and 17, we employed a constant value of g; $g = 0.6$. This gave quite good agreement with the measured ϵ_ν (Fig. III.5.3). Later we calculated g (15),

$$g = \int_0^\pi p \cos \theta \, d\Omega \quad (19)$$

where p is the phase function. In all calculations we used a variety of particle size distributions, all of the log-normal type. The distributions are characterized by the location of the diameter of maximum population and by the width of the distribution, σ .

In this two-stream model, the calculated emissivity (= absorbance efficiency) is a slowly varying function of particle size distribution, as shown in Fig. III.5.4. With an appropriate particle size distribution, the calculated emissivity is in good agreement with the measured spectrum (Fig. III.5.3).

Monte Carlo Method

In this method, a random array of particles from the chosen size distribution constitute the sample. Monte-Carlo techniques are used to follow the paths of photons as they scatter from particle to particle. The particle size is chosen from the distribution by random number generation, and the probability for absorption, and for scattering into each 10° angular increment, are looked-up from tables prepared previously. These probabilities are used in the normal way to determine the outcome of the encounter. The trajectory of each entering photon has two possible outcomes.: it can be terminated by an absorption event, or it can re-emerge as a reflected ray. Some trajectories for entering photons are displayed in Fig. III.5.5 which indicates the probability of an absorption event is greater for radiation at low wavenumbers. Again, for one choice of particle size distribution the calculated emissivity agrees well with the measured spectrum (Fig. III.5.6). The optimum particle distribution for this model was indistinguishable from the optimum for the two stream model. It is noted that the Monte Carlo technique has wider applicability than the two-stream model, although in the present instance both are applicable, and both describe the data well.

Figure III.5.3. Measured Emittance Compared to Prediction for a Ground Sample of Sintered Slag #1.

Figure III.5.4. Predicted Emittance by the Two-Stream Model as a Function of Particle Size Distribution. (c) Shows the Best Agreement with the Measured Emittance of Fig. III.5.3.

Figure III.5.5. Example Trajectories for 150 Photons Entering a Slab of Ground Slag (particle diameter = 1 μm) as Predicted by a Monte Carlo Model for Three Distinct Spectral Wavenumbers.

Figure III.5.6. Predicted Emittance by the Monte Carlo Model as a Function of Particle Size Distribution. (d) Shows the Best Agreement with the Measured Emittance of Fig. III.5.3.

IV. CONCLUSIONS AND RECOMMENDATIONS

This research program has demonstrated that the radiative properties (i.e. emissivity, reflectivity, and transmittivity) of extracted ash and slag combustion deposits at elevated temperature can routinely be measured in the laboratory. The technique combines spectroscopic measurements of radiance and reflectance/transmittance in the mid IR, between 1.6 and 20 μm , to determine the emissivity and the temperature at which the measurements were made.

The results have shown that the radiative properties are highly dependent on the morphology of the combustion deposit. This observation was then used to explore three morphology dependent predictive models which were shown to compare well with measured emissivities.

Fused slag deposits, which exist as relatively smooth surfaced slabs, exhibited a high spectral emittance (≥ 0.9) over a wide temperature range (300 K to 1630 K). These measurements included the slag in both the solid and molten state.

Sintered slag deposits, due to their particle-like morphology, exhibited a wavelength dependent drop in emittance. In the long wavelength spectral region where the chemical species of the slag were shown to absorb IR radiation, the emittance remained high. The energy scattering efficiency of the sintered morphology, however, increased toward shorter wavelength energy and hence demonstrated lower emittance values. The degree of sintering, that is, to what extent the surface is particle-like and not slab-like, controls the extent of emittance deviation from near black-body character.

Fly ash deposits, which consists of fine packed particles, demonstrated the largest wavelength dependent excursions (down to $\epsilon_\nu = 0.45$) due to the relatively high scattering efficiency of the deposits.

Based on the results of this research program it can be concluded that the rate of transfer of energy between surfaces and flames in a boiler or furnace environment will be greatly effected by the surface morphology of combustion deposits. The work presented here also demonstrated that thin layers ($< 200 \mu\text{m}$) of deposit were sufficient to completely influence the interaction of incident radiation.

An obvious extension of this work would be to utilize the developed techniques for in-situ boiler and furnace measurements of emissivities and temperatures. A research proposal has been submitted to the Department of Energy under the SBIR program which addresses this application.

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APPENDIX A

SUPPLEMENT TECHNIQUE VALIDATION RESULTS

APPENDIX A - SUPPLEMENT RESULTS

Sample Class A

Synthetic Sapphire: partially transmitting, specular reflecting, Christiansen dip

The Sapphire optical window allowed for the spectral emittance to be determined by both closure (Fig. A1) and the Christiansen dip (Fig. A3) techniques. Excellent agreement is demonstrated between the two methods and with emittance derived from the literature.

Polished Silicon Nitride: non-transmitting, specular reflecting, Christiansen dip

Back-heating samples with an oxygen/acetylene torch produced the highest observed surface temperatures in the Phase I program. Figure A4 demonstrates temperature and emittance determination for polished Si_3N_4 heated with the $\text{O}_2/\text{C}_2\text{H}_2$ torch by the Christiansen dip method. The shape of our emittance curve follows trends reported by Johnson, et al. (2) Fig. A4c) who observed a maximum at $\sim 8 \mu\text{m}$ followed by a sharp decline and then increase to $14 \mu\text{m}$. Johnson's data was taken at 1700 K. Our surface was measured at 1475 K.

Sandblasted Silicon Nitride: non-transmitting, diffuse (isotropic) reflecting, Christiansen dip

After sandblasting the rough Si_3N_4 sample that displayed anisotropic reflection, the surface exhibited isotropic reflection. Figure A5 indicates the agreement in angular reflectance for two rotational orientations of the surface with respect to the plane of incident and collected IR radiation. The spectral emittance as determined by closure shows a slightly different shape than the emittance for the original surface shown in Fig. A6c for cercom Si_3N_4 .

Sample Class B

Rough Silicon Nitride: non-transmitting, diffuse (isotropic) reflecting, Christiansen dip

A comparison of Si_3N_4 from different manufactures is shown in Fig. A6, with the temperature and spectral emittance determined by the Christiansen dip method. The general shape of the two emittance spectra are similar, but a definite shift of where the emittance is unity (i.e., zero reflectance) is observed. Cercom characterizes this grade of Si_3N_4 as B-phase having a grain size of $0.35\text{--}0.50 \mu\text{m}$. The Norton sample is characterized as B-phase with $3.0 \mu\text{m}$ grain size. At this point we are not sure of what fundamental properties of the two Si_3N_4 samples accounts for the spectral shift, but it is significant that our technique allows for the distinction between the two materials to be observed.

Rough Silicon Carbide: non-transmitting, diffuse (isotropic) reflecting, Christiansen dip

Figures A7-A9 pertain to the same surface as SiC at two separate temperatures. The Christiansen dip method was used to measure temperatures of 1075 K and 1421 K. Figure A9a indicates negligible change in the spectral emittance between these temperatures. Figure A9b is emittance data from Johnson et al. (2) for several SiC samples at 1900 K. Shape of the literature data is similar to ours with a maximum just above $10 \mu\text{m}$.

Sample Class C

AlSiMag Ceramic: partially-transmitting, diffuse reflecting, Christiansen dip

This alumina-silica-magnesium ceramic exhibited multiple internal scattering of the incident radiation as was described for Al_2O_3 . The Christiansen dip method (Fig. A10) determined a surface temperature that was 33 K less than that indicated by a thermocouple that was bonded to the surface. The spectral emittance for this material has a shape similar to the Coors' alumina sample (see Fig. II.4.11), although the other elemental components in the AlSiMag exhibit unique features.

Al₂O₃ Layer on Aluminum (Anodized Aluminum): partially-transmitting, diffuse reflecting, Christiansen dip

The surface temperature determined by the Christiansen method (Fig. A11) was within 2 K from the temperature indicated by a surface bonded thermocouple. A shift in the Christiansen dip spectral region is observed when compared to the slab of Al₂O₃ (compare to Fig. II.4.12), and a distinct rise in emittance is exhibited at $\sim 3500 \text{ cm}^{-1}$.

Quartz Quilt (Shuttle AFRSI): partially-transmitting diffuse reflecting, Christiansen dip

This sample was a woven quartz quilt that was attached to what appeared to be a quartz fiber plug. It was very difficult to be sure that the surface was aligned correctly for the specular geometry. Figure A12a shows the low amount of reflected energy after maximizing the detector signal by the alignment procedure. The Christiansen dip method determined a surface temperature of 682 K, which was 15 K lower than the temperature indicated by a thermocouple placed between the quilt and the plug. One would expect the thermocouple to indicate a slightly higher temperature since it was insulated by its placement between layers of material. The spectral emittance of this sample (Fig. A12c) displayed features similar to that of the optical grade fused quartz (see Fig. II.4.5c), including a similar spectral region where $\epsilon = 1.0$ and hydroxyl impurities at 3650 cm^{-1} and 4500 cm^{-1} .

Figure A-1. Spectral Emittance Calculated from IR Reflectance and Transmittance Measurements for Synthetic Sapphire at $\sim 1000\text{K}$. a) Reflectance, b) Transmittance, and c) Emittance = $1 - \text{Reflectance} - \text{Transmittance}$. The Darkened Circles Overlaid in the Non-Transparent Spectral Region in (c) were Calculated from 1-Eq. (12) using the Optical Constants shown in Figure A-2.

Figure A-2. Optical Constants of Sapphire. The Ordinate Represents Either n or k . Solid Line n , Dashed Line is k . (From Ref. 25).

Figure A-3. Surface Temperature and Spectral Emittance of Synthetic Sapphire Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Radiance Overlaid with a 965K Theoretical Black-body Curve, b) Emittance = Radiance/BB_{965K} and c) Comparison of Emittance in b) to Emittance = 1 - Reflectance - Transmittance.

Figure A-4. Surface Temperature and Spectral Emittance of Cercom Polished Silicon Nitride Determined by Radiance Measurement and Zero Reflection/Transmission Feature.
a) Radiance Overlayed with a 1475K Theoretical Black-body Curve, b) Emittance = Radiance/BB_{1475K} and c) Data of Johnson et al., (2) for Several Si₃N₄ Samples at 1700K.

Figure A-5. Comparison of Reflectivity and Emittance at ~1050K for Two Rotational Orientations of Sandblasted Cercom Silicon Nitride. a-b) Directional Integrated Components of Reflectivity, c) Total Hemispherical Reflectivity for Both Cases and d) Emittance = 1-Reflectance for Both Cases.

Figure A-6. Surface Temperature and Spectral Emittance Determination from Radiance and Zero Reflection/Transmission Feature for Different Silicon Nitride Samples. a) Radiance Overlayed with a Theoretical Black-body Curve Corresponding to the Surface Temperature for Cercom Rough Si₃N₄, b) Radiance Overlayed with a Theoretical Black-Body Curve Corresponding to the Surface Temperature for Norton Rough Si₃N₄ and c) Comparison of Emittance = Radiance/BB(T) for Each Surface.

Figure A-7. Surface Temperature and Spectral Emittance of Carborundum Hexaloy SA Silicon Carbide Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 1075K Theoretical Black-body Curve, and c) Emittance = Radiance/BB_{1075K}.

Figure A-8. Surface Temperature and Spectral Emittance of Carborundum Hexaloy SA Silicon Carbide Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 1421K Theoretical Black-body Curve, c) Emittance = Radiance/ $\text{BB}_{1421\text{K}}$.

Figure A-9. a) Comparison of Spectral Emittance for Carborundum Hexaloy SA Silicon Carbide at 1075K and 1421K. b) Data of Johnson et al. (2) for Several SiC Samples at 1900K.

Figure A-10. Surface Temperature and Spectral Emittance of ALSIMAG (alumina-silica-magnesium ceramic) Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Integrated and Summed Reflectance from 15° (specular) to 45° , b) Radiance Overlayed with a 1120K Theoretical Black-body Curve and c) Emittance = Radiance/BB_{1120K}. A 0.005" Thermocouple Bonded to the Surface Indicated a Temperature of 1153K.

Figure A-11. Surface Temperature and Spectral Emittance of Anodized Aluminum Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 710K Theoretical Black-Body Curve, and c) Emittance = Radiance/BB 710K. A Surface Bonded Thermocouple Indicated a Temperature of 712K.

Figure A-12. Surface Temperature and Spectral Emittance of Shuttle AFRSI (woven quartz quilt) Determined by Radiance Measurement and Zero Reflection/Transmission Feature. a) Reflectance at the Specular Angle, b) Radiance Overlayed with a 682K Theoretical Black-Body Curve, and c) Emittance = Radiance/682K. A Thermocouple Placed Behind the First Layer of Material Indicated a Temperature of 697K.

APPENDIX B

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